Flexible Coordination of N,P-Donor Ligands in Aluminum Dimethyl and Dihydride Complexes

Flexible coordination of N,P-Donor Ligands in Aluminum Dimethyl and Dihydride Complexes

*Rosalyn L. Falconer, Gary S. Nichol, Michael J. Cowley**

School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK

ABSTRACT.

Aluminum hydrides, once a simple class of stoichiometric reductants, are now emerging as powerful catalysts for organic transformations such as the hydroboration or hydrogenation of unsaturated bonds. The coordination chemistry of aluminum hydrides supported by phosphorus donors is relatively underexplored. Here, we report aluminum dihydride and dimethyl complexes supported by amido-phosphine ligands, and study their coordination behavior in solution and in the solid state. All complexes exist as κ^2-*N,P* complexes in the solid state. However, we find that for amidophosphine ligands bearing bulky aminophosphine donors, aluminum dihydride and dimethyl complexes undergo a 'ligand-slip' rearrangement in solution to generate κ^2-*N,N* complexes. Thus, importantly for catalytic activity, we find that the coordination behavior of the phosphorus donor can be modulated by controlling its steric bulk. We show that the reported aluminum hydrides catalyze the hydroboration of alkynes by HBPin, and that the variable coordination mode exhibited by the amidophosphine ligand modulates catalytic activity.

Introduction

Aluminum hydrides such as $LiAlH_4$, RedAl (sodium bis(2-methoxyethoxy)aluminum hydride) and AlH_3 are ubiquitous in synthetic chemistry for their use as reducing agents.[1] Recently, the scope of reactivity of these simple aluminum hydrides has been expanded into the catalytic hydroboration of alkenes and alkynes; a development of significant environmental and economic importance due to the high abundance and relatively low toxicity of aluminum compared to platinum group metals.[2-3] Numerous other uncomplicated aluminum hydride compounds are also capable of the hydroboration or even hydrogenation of unsaturated polar bonds such as aldehydes, ketones or imines.[4-5] Aluminum hydride compounds with more complex ligands have also been investigated. For example, *N*-heterocyclic imine-coordinated aluminum hydrides catalyze carbonyl hydroboration[6] whilst the β-diketiminate stabilized aluminum dihydride **I** (Figure 1), also catalyzes the hydroboration of alkynes.[7] The dihydride **I** is also a precursor to β-diketiminate stabilized Al(I) species (at least within the coordination sphere of a transition metal).[8]

Reported aluminum dihydride complexes overwhelmingly use nitrogen donor ligands (e.g. **I-III**, Figure 1).[9-13] Typically, these ligands are also multi-dentate (to stabilize the intrinsically electron poor aluminum center) and sterically hindered, in order to prevent dimerization or oligimerization by bridging interactions. In coordination chemistry, ligands greatly influence the chemistry at the metal center. Thus, the investigation and development of aluminum hydride chemistry using a diverse array of ligand classes is essential for the expansion of aluminum hydride chemistry and catalysis.

Aluminum dihydrides or related species with phosphorus-based ligands are much rarer. A few examples of dimethyl aluminum complexes with mixed-donor ligands are known, in which

bidentate ligands having one nitrogen donor also contain a "soft" donor, such as sulfur or phosphorus (**IV** and **V**, Figure 1).[14-18] The likely more labile aluminum-phosphorus interaction offers the possibility of hemilability, which can be useful in the stabilization of catalytic transition or resting states.[19] Indeed, Fryzuk *et al.* used NMR spectroscopy to demonstrate the fluxional coordination of the phosphorus donor atoms in **V**, resulting in an equilibrium between 4- and 5-coordinate aluminum centers.[20]

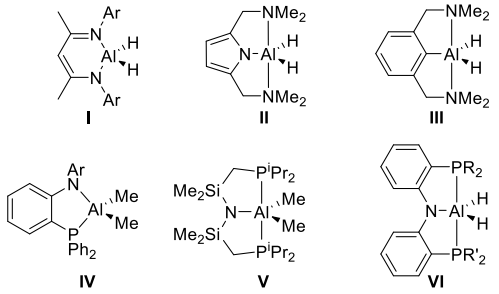


Figure 1: Literature examples of aluminum dihydride and dimethyl complexes stabilized by nitrogen based ligands (**I-III**) or mixed donor ligands (**IV-VI**).[9-11, 15, 20-21] (**I**, **IV**: Ar = 2,6-$C_6H_3{}^iPr_2$, **VI**: R = R' = Ph, ^{i}Pr or R = Ph, R' = ^{i}Pr).

In comparison to mixed-donor methyl complexes, mixed-donor aluminum dihydride complexes are scarce, with only a single example.[21] Most phosphorus-coordinated aluminum hydrides are limited to simple adducts between phosphines and alane, with the exception of **VI** (Figure 1), reported by Liang *et al.* in 2009, which was synthesized *via* the reduction of the corresponding aluminum dichloride using $LiAlH_4$.[21-22] Hemilability of the phosphorus donors was not found in this example, likely due to the rigidity of the ligand backbone.

Herein, we describe novel aluminum dimethyl and dihydride species stabilized by mixed *N,P*-donor ligands that display flexible coordination modes based on a 'ligand-slip' phenomenon.

Results and discussion

The amido-phosphine ligands **1a-c** [23] (Figure 2) have previously been used to prepare nickel and palladium complexes, as well as to support reactive Si(II) compounds.[24-27] The steric bulk around both nitrogen and phosphorus centers of **1a-c** has not only enabled the isolation of reactive species such as Si(II) hydrides, but also modulates reversible Si(II)/Si(IV) oxidative additions/reductive eliminations. At the phosphorus donor in particular, both steric bulk and electron donating ability are readily tunable. We were interested whether this class of ligands could be employed to support aluminum centers and whether they could be used to modulate their structure and reactivity.

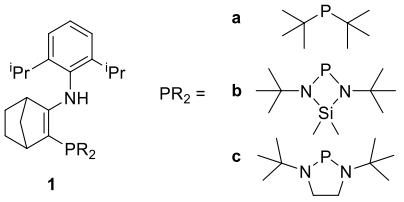
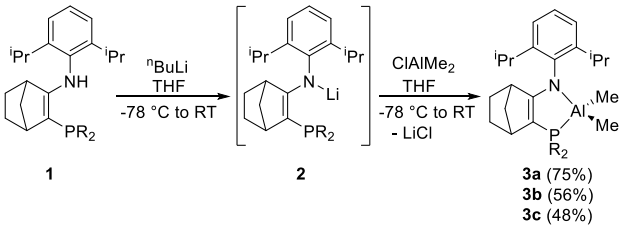


Figure 2: Mixed donor ligands **1a-c**

Synthesis and solid-state structures of dimethyl aluminum complexes. Dimethylaluminum complexes are a broad class of compounds that have been reported as catalysts or cocatalysts in alkene polymerisation.[28-30] Complexes of dimethyl aluminum stabilized by many nitrogen or mixed donor ligands have been reported, rendering this class of compounds ideal for benchmarking the coordination abilities of ligands **1a-c**. We decided to first investigate the coordination of ligands **1** to dimethyl aluminum moieties.

The coordination of **1b** and **1c** to silicon(IV) centers has been reported and was achieved by deprotonation before treatment with the appropriate silicon halide.[27] Accordingly, ligands **1a-c** were deprotonated with ^{n}BuLi at -78 °C to afford yellow solutions of **2a-c** (Scheme 1). A characteristic resonance is observed in $^{31}P\{^{1}H\}$ NMR spectra of these solutions in the form of a 1:1:1:1 quartet upfield compared to the free ligand. The 1:1:1:1 multiplicity indicates coordination

to lithium (e.g. **2a** $^{31}P\{^{1}H\}$ NMR: δ 10.9 ppm, J_{PLi} = 54 Hz). Similarly, in the ^{7}Li NMR spectra, doublets are observed due to coupling with phosphorus (e.g. **2a** ^{7}Li NMR: δ 1.3 ppm, J_{LiP} = 54 Hz).



Scheme 1: Lithiation of ligands **1** to form **2** followed by reaction with dimethylaluminum chloride to form dimethyl aluminum complexes **3a-c**.

The dimethyl aluminum complexes **3a**-**c** were obtained by reaction of the in-situ generated lithiated ligands **2** with 1 equivalent of dimethylaluminum chloride. Extraction of the products in pentane, followed by filtration and evaporation of the solvent afforded **3a**-**c** as yellow air-sensitive solids. Complexes **3a** and **3c** could be isolated as analytically pure solids by crystallization, whilst **3b** was clearly identified but resisted purification attempts. All three complexes **3a**-**c** were extremely sensitive to air and moisture.

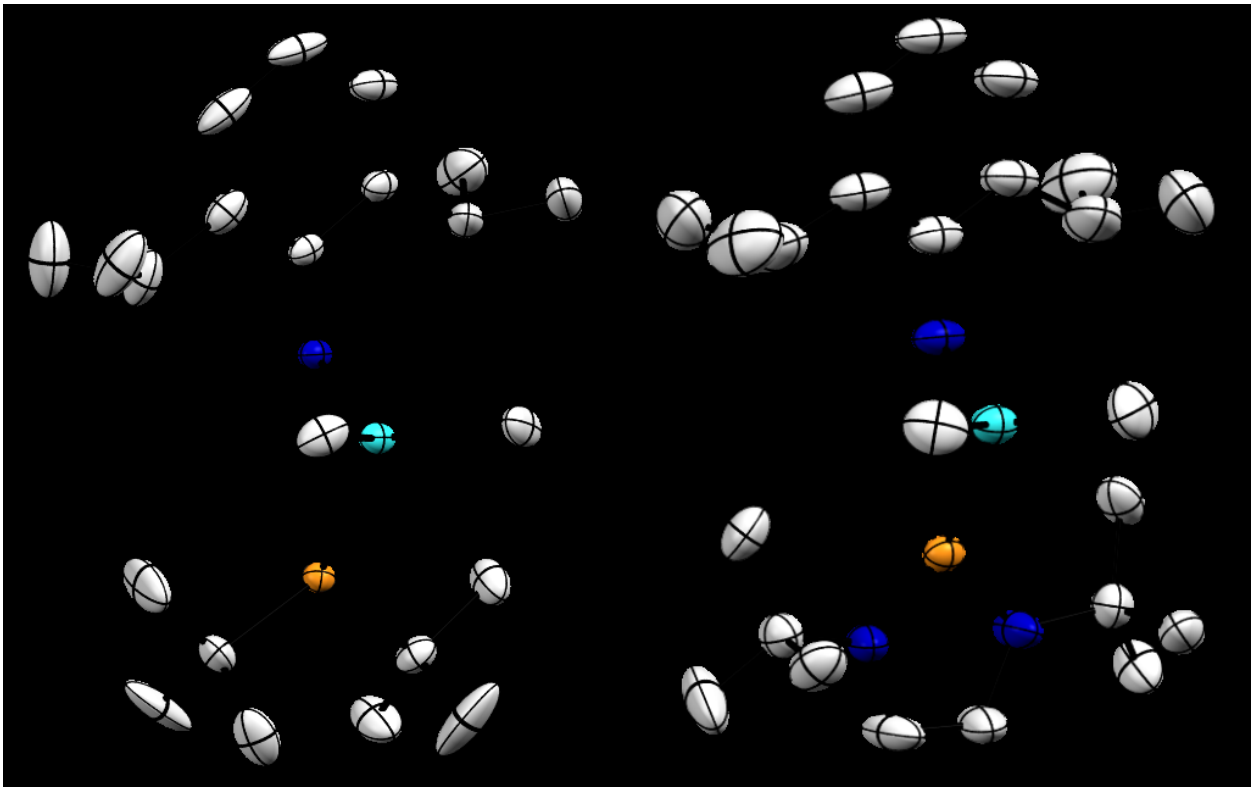


Figure 3: Molecular structure of **3a** (left) and **3c** (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and disordered ligand atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **3a**: N(1)-Al(1) 1.895(14), P(1)-Al(1) 2.4800(6), Al(1)-C(1) 1.9652(19), Al(1)-C(2) 1.970(2), N(1)-Al(1)-P(1) 86.67(4), N(1)-Al(1)-C(1) 116.12(8), N(1)-Al(1)-C(2) 115.25(8), P(1)-Al(1)-C(1) 114.53(7), P(1)-Al(1)-C(2) 114.00(7), C(1)-Al(1)-C(2) 109.00(9); **3c**: N(1)-Al(1) 1.917(3), P(1)-Al(1) 2.5304(9), Al(1)-C(1) 1.967(4), Al(1)-C(2) 1.964(4), N(1)-Al(1)-P(1) 85.59(8), N(1)-Al(1)-C(1) 116.14(19), N(1)-Al(1)-C(2) 116.19(19), P(1)-Al(1)-C(1) 115.98(13), P(1)-Al(1)-C(2) 115.99(14), C(1)-Al(1)-C(2) 106.4(2).

The solid-state structures of **3a** and **3c** were determined by X-ray crystallography (Figure 3). Both compounds have a tetrahedral aluminum center with coordinated nitrogen and phosphorus donors forming a planar ring. The ring is heavily skewed with (as might be expected) a substantially shorter interaction between aluminum and the N-donor than with the phosphine (e.g.

3a, Al(1)–N(1) 1.8985(14) Å vs Al(1)–P(1) 2.4800(6) Å). Both Al–N and Al–P distances are comparable to those previously reported, for example the *N,P*-coordinated dimethyl aluminum complex **IV** (Al–N 1.894(6) Å, Al–P 2.477(3) Å).[15]

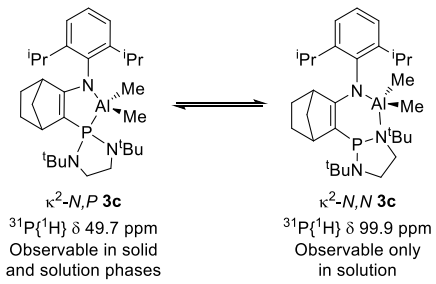
The Al–N bond distances of **3a** and **3c** are indistinguishable, but the Al–P bond length is slightly longer in the latter at 2.5304(8) Å, indicating the phosphorus is less strongly bound to the aluminum center. The aminophosphine donor of **3c** is more electron donating than the dialkylphosphine of **3a**, which would be expected to give rise to the opposite trend.[31] The origin of the difference is likely due to steric effects: the greater steric bulk in **3c** prevents the close approach of the phosphine to the aluminum center. Indeed, this can be observed in the C(1) –Al(1) –C(2) angle, which is smaller in the case of **3c** (106.4(2)°) than **3a** (109.00(9)°) despite the similar bite angles of the two (**3a**, 86.67(4)°; **3c**, 85.59(8)°).

Solution behavior of 3a-c. Despite their similar solid-state structures, in the solution phase NMR spectroscopy revealed differences in coordination behavior between the dimethylaluminum complexes **3a-c**. No signals were observed for any of the compounds by ^{27}Al NMR spectroscopy.

NMR spectroscopy of dimethylaluminum complexes **3a** and **3b** was consistent with the solid-state structure determined for **3a**. $^{31}P\{^{1}H\}$ NMR spectroscopy revealed a single resonance for each (**3a**: 1.6 ppm, **3b**: 64.0 ppm) shifted upfield compared to the respective free ligand resonances ($\Delta\partial$(**3a**) = -54.4 ppm; $\Delta\partial$(**3b**) = -83.3 ppm). The $^{31}P\{^{1}H\}$ resonances for **3a** and **3b** were also significantly broadened in comparison to free ligands **1a** and **1b**, presumably as a result of coordination of the phosphorus to the quadrupolar (I = 5/2) aluminum nucleus (**3a** full width at half maximum ($\Delta\nu_{1/2}$) = 21.1 Hz, **1a** = 2.7 Hz).

In the ^{1}H NMR spectra of **3a** and **3b**, resonances corresponding to the aluminum methyl groups appear as doublets arising from coupling to phosphorus (**3a**: -0.33 and -0.19 ppm, $^{2}J_{HP}$ = 2.5 Hz). The ^{1}H NMR spectrum also shows that each CH_3 group in the Dipp substituent is inequivalent, indicating restricted rotation likely due to steric constraints.

Crystalline **3c** was also characterized by solution phase NMR spectroscopy. Surprisingly, the ^{31}P{^{1}H} NMR spectrum contained two resonances, at 99.9 ppm and 49.7 ppm in a ratio of 3:2 (the same ratio was observed by ^{1}H NMR spectroscopy). The resonance at 49.7 ppm is broadened ($\Delta\nu_{½}$ = 47.5 Hz) and downfield ($\Delta\partial$ = -40.9 ppm) from that of **1c**, so is consistent with coordination of the phosphorus to the aluminum center as in **3a** and **3b**. Conversely, the resonance at 99.9 ppm is sharp ($\Delta\nu_{½}$ = 5.3 Hz) and close in chemical shift to that of the free ligand **1c** ($\Delta\partial$ = +9.3 ppm), which indicates the phosphorus in this environment is not coordinated to the aluminum center.



Scheme 2: Proposed structures of κ^2-*N,P* and κ^2-*N,N* **3c**. In the solid state, only κ^2-*N,P* **3c** is observed, whilst in solution, both κ^2-*N,P* and κ^2-*N,N* isomers are observed.

On the basis of the ^{31}P NMR spectroscopic data, and by analogy with the behavior more fully studied in the hydride analogue **5c** (see below), we propose that **3c** exists in two forms in solution, in which the ligand exhibits a variable coordination mode, having either κ^2-*N,P* or κ^2-*N,N* coordination. In the solid state, κ^2-coordination is exclusively observed. In solution, however, the two isomers are present as a result of the flexible coordination mode of the ligand.

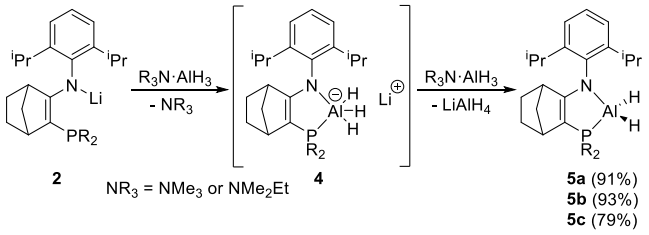
The ^{1}H NMR spectrum of **3c** is consistent with both κ^2-*N,P* and κ^2-*N,N* isomers existing in solution, with two sets of resonances present in a ratio of 57:43 (consistent with the 3:2 ratio observed by ^{31}P NMR). Multinuclear 2-D NMR spectroscopic experiments verified that in both isomers the ligand backbone was intact and undisturbed. The possibility of a dimeric κ^1-*N* isomer of **3c** (with e.g. bridging methyl ligands) was excluded based on an analysis of the ^{1}H DOSY NMR spectrum, which indicated that both the observed isomers diffused at the same rate in solution. Similarly, high resolution mass spectrometry also identified the product as **3c** with no evidence of a dimeric species observed.

Synthesis of aluminum dihydride complexes. Following the preparation of the dimethyl aluminum complexes **3a-c**, we turned our attention to the preparation of aluminum dihydride complexes. Ligands **1a-c** do not react with $Me_2EtN{\cdot}AlH_3$, in contrast to the observed reactivity of amidine ligands which evolve H_2 and form aminidinato aluminum dihydrides.[32] Treatment with $LiAlH_4$ also had no effect. Thus, we used the lithiated ligands **2a-c** as precursors instead.

Treatment of **2b** with a single equivalent of $Me_2EtN{\cdot}AlH_3$ resulted in a yellow solution, the ^{31}P NMR spectrum of which revealed a quartet (110.8 ppm, $^{2}J_{PH}$ = 34 Hz) which collapsed to a singlet in the $^{31}P\{^{1}H\}$ spectrum. This evidence, as well as further characterization by multinuclear NMR spectroscopy and mass spectrometry, confirmed the formation of aluminate complex **4b** (Scheme 3).

The addition of a second equivalent of $Me_2EtN{\cdot}AlH_3$ to solutions of **4b** was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy, which revealed complete consumption of **4b** and formation of a new species represented by a broad singlet (61.3 ppm, $\Delta\nu_{1/2}$ = 55.7 Hz), indicating phosphorus coordination to aluminum. Analysis of the ^{27}Al NMR spectrum revealed the formation of $LiAlH_4$. Based on this evidence, the reaction pathway shown in Scheme 3 is proposed: reaction of **2b** with

$Me_2EtN{\cdot}AlH_3$ proceeds by forming **4b** by displacement of the amine from $Me_2EtN{\cdot}AlH_3$. The second equivalent of $Me_2EtN{\cdot}AlH_3$ abstracts a hydride from **4b**, generating **5b**, $LiAlH_4$, and eliminating the amine.



Scheme 3: Proposed mechanism for the reaction of **2** with $Me_2EtN{\cdot}AlH_3$ (NR_3 = NMe_3 or NMe_2Et) to form aluminum dihydride **5** *via* charged intermediate **4**.

When **2a** was treated with 1 equivalent of $Me_2EtN{\cdot}AlH_3$, the resulting pale yellow solution was revealed to contain a mixture of compounds by $^{31}P\{^1H\}$ NMR spectroscopy. In addition to residual lithiated ligand **2a**, equal quantities of the aluminate intermediate **4a** (8.0 ppm) and the neutral aluminum dihydride **5a** (-10.1 ppm) were observed. $LiAlH_4$ was also observed by ^{27}Al NMR spectroscopy. The 2:1:1 ratio of the three species reveals that the lithiated ligand **2a** and the intermediate aluminate **4a** react at comparable rates with $Me_2EtN{\cdot}AlH_3$ to generate the statistical mixture. This contrasts to the situation for **4b**, where hydride abstraction by $Me_2EtN{\cdot}AlH_3$ is much slower than its coordination to lithiated ligand **2b**. Upon addition of a second equivalent of $Me_2EtN{\cdot}AlH_3$ to **4a**, the reaction mixture turned colorless and the $^{31}P\{^1H\}$ NMR spectrum showed complete conversion to **5a** (7.5 ppm).

Preparatively, the dihydride complexes **5a-c** were obtained in multi-gram quantities from treatment of the lithiated ligands **2a-c** with 2 equivalents of $Me_3N{\cdot}AlH_3$ or $Me_2EtN{\cdot}AlH_3$. All three

compounds could be isolated as colorless solids in excellent yields of 80-90 %. Dihydrides **5b** and **5c** could be further purified by crystallization from hexane.

In the ^{1}H NMR spectra of **5a** and **5b**, Al-H resonances are visible as very broad singlets at 4.6 ppm (**5a**, $\Delta\nu_{½}$ = 71.6 Hz; **5b** $\Delta\nu_{½}$ = 125.3 Hz), due to the influence of the quadrupolar aluminum atom. Despite the lower steric influence of the hydride ligands compared to the methyl ligands of **3a** and **3b**, the methyl groups of the Dipp-substituent remain inequivalent, indicating continued restricted rotation. Compound **5c** has more complex solution behavior that will be discussed below.

IR spectroscopy of solid-state samples of **5a-c** revealed the expected symmetric and antisymmetric Al-H stretches (**5a**: 1810, 1786; **5b** 1831, 1816; **5c** 1825, 1801 cm^{-1}) for a four coordinate aluminum dihydride center.[33-34]

Solid state structures of 5b and 5c. The structures of **5b** and **5c** were verified by X-ray diffraction (Figure 4). Broadly, the structures are analogous to those of **3a** and **3c**. The amido-phosphine ligand in each compound is κ^2-*N,P* coordinated, which together with the hydride ligands (located using a difference map and allowed to refine freely) results in a tetrahedral environment at the aluminum center. The two structures have statistically identical N–Al bond distances (**5b**: 1.8972(15) Å; **5c**: 1.892(2) Å) which are essentially identical to those observed for the dimethyl analogues **3a** and **3c**. A more substantial difference is observed in the P–Al bond distances, which for the dihydride **5c** is shorter than in the corresponding dimethyl complex **3c** (Al(1)–P(1) **5c** 2.4791(10) Å, **3c** 2.5304(8) Å). The contraction of this bond can be explained by the smaller size of the hydride substituents. Similarly, a comparison between the two dihydrides **5b** and **5c** reveals a shorter Al(1)–P(1) distance for **5b** as a result of reduced bulk at the phosphorus center in comparison to **5c** (**5b** 2.4442(7) Å, **5c** 2.4791(10) Å). The larger bite angles for the dihydrides **5b**

and **5c** [**5b** (87.47(5)°), **5c** (86.60(6)°)] compared to the dimethyl compounds is also due to the smaller hydride substituents compared to methyl groups.

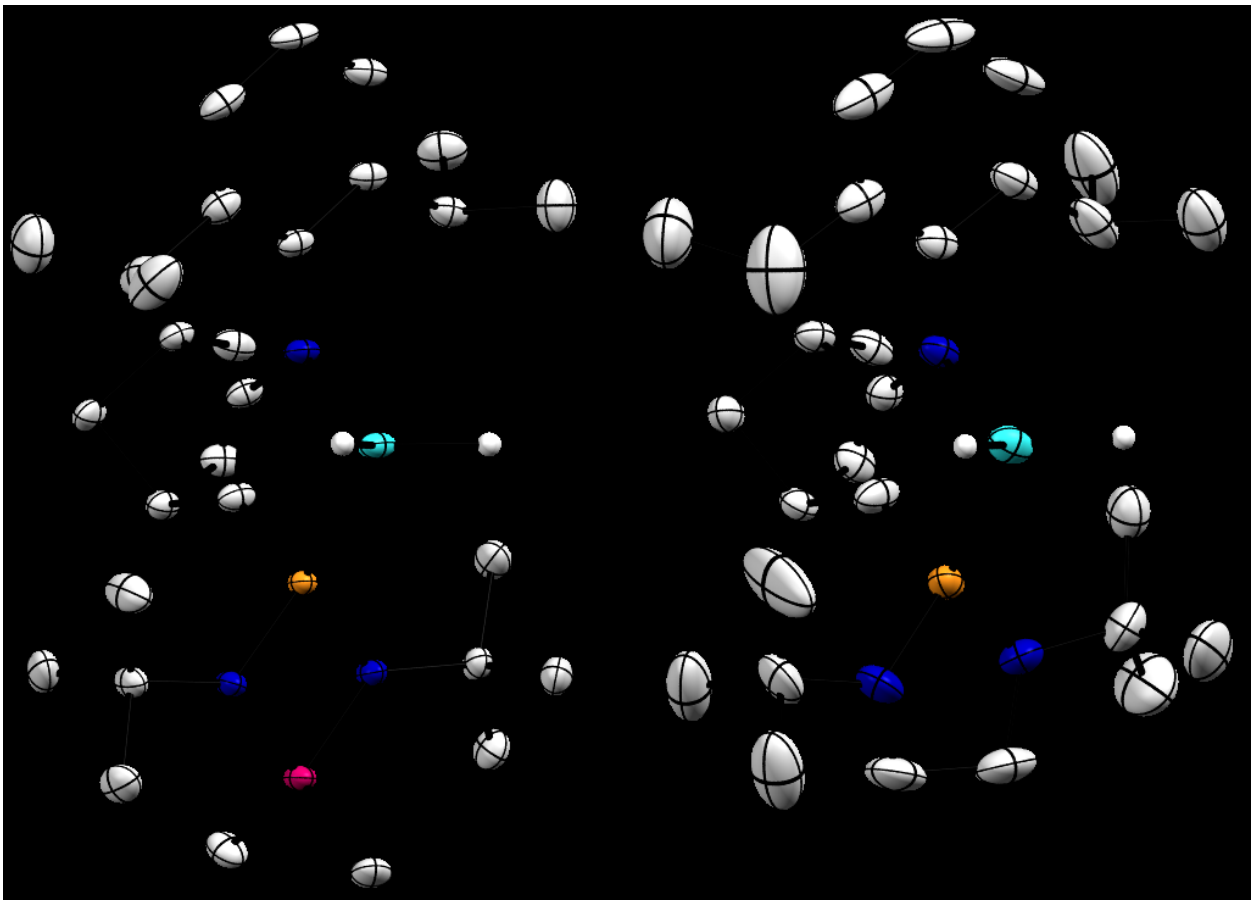
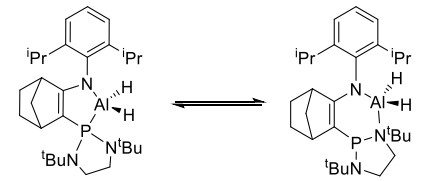


Figure 4: Molecular structures of **5b** (left) and **5c** (right). The aluminum hydride atoms were located using a difference map and allowed to refine freely. Ligand hydrogen atoms and disorder omitted for clarity. Selected bond lengths (Å) and angles (deg.) **5b**: N(1)-Al(1) 1.8972(15), P(1)-Al(1) 2.4442(7), N(1)-Al(1)-P(1) 87.47(5); **5c**: N(1)-Al(1) 1.892(2), P(1)-Al(1) 2.4790(10), N(1)-Al(1)-P(1) 86.60(6)

Solution Phase NMR Characterization of 5c. Like its dimethyl analogue **3c**, the dihydride **5c** exhibits variable coordination modes in solution. Upon dissolution of crystalline **5c**, the $^{31}P\{^{1}H\}$ NMR spectrum revealed the presence of two broad singlets at 96.9 ppm ($\Delta\nu_{½}$ = 137.9 Hz) and 47.8 ppm ($\Delta\nu_{½}$ = 96.6 Hz) in a ratio of 1:2. By ^{1}H NMR, two sets of resonances were also observed for all proton environments, including the dihydride ligands (signals at κ^2-*N,N* **5c** 4.3 ppm, κ^2-*N,P* **5c** 4.6 ppm. The ratio of the two species as measured by ^{1}H NMR in a ratio of 35:65, consistent with that observed in the ^{31}P NMR spectrum).



Scheme 4: Proposed structures of κ^2-*N,P* and κ^2-*N,N* **5c**. In the solid state, only κ^2-*N,P* **5c** is observed, whilst in solution both κ^2-*N,P* and κ^2-*N,N* isomers are observed.

The two solution-phase isomers of **5c** were determined to be κ^2-*N,P* **5c**, as observed in the solid state, and a κ^2-*N,N* isomer in which the phosphine ligand has 'slipped' and coordinates through one of the phosphorus-bound nitrogen atoms (Scheme 4). Evidence for the κ^2-*N,N* coordination mode is as follows:

1. The two isomers are both monomeric species, as revealed by ^{1}H-DOSY measurements which indicate similar diffusion coefficients. Thus, we were able to rule out the presence of a dimeric species with bridging hydrides (consistent with solution- and solid-phase IR spectroscopy which did not reveal evidence of bridging hydride ligands).
2. In the $^{31}P\{^{1}H\}$ NMR spectrum, the resonance at 96.9 ppm is assigned to the κ^2-*N,N* isomer due to its similarity to that observed for the free ligand **1c** (90.6 ppm), which indicates the

phosphorus center is not coordinated to aluminum. The resonance at 47.8 ppm is assigned to the κ^2-*N,P* isomer observed in the solid state (confirmed by solid-state NMR measurements – see below).

3. The aluminum-hydride stretching frequencies recorded for **5c** in solution (1823 cm^{-1}) and in the solid-state (1825, 1801 cm^{-1}) are consistent with a four-coordinate aluminum dihydride species in both phases, ruling out a κ^1-*N* isomer in which the phosphine is uncoordinated.
4. Using DFT we performed geometry optimization and frequency calculations on κ^2-*N,P* isomers of **5a-5c** at the and M062X/Def2SVPP and M062X/6,31G+(d,p)/Lanl2DZ levels (table S1). Following the lead of Crimmin *et al.*, we found that calculations using the split basis set were essential to replicate experimentally observed Al–H stretching frequencies.[33] The calculations accurately reproduced the experimentally observed geometries and IR stretching frequencies for **5a-c**, enabling us to use this computational methodology to assign the identity of the solution-phase isomer of **5c**.
5. A relaxed potential energy surface (PES) scan of **5c** in which the Al–P distance was increased systematically starting from the κ^2-*N,P* geometry revealed two potential minima (Figure S1), which were reoptimized at the M062X/6,31G+(d,p)/Lanl2DZ level (Figure 5, Table S2). A κ^1-*N* isomer was found to be 22.6 kcal mol^{-1} higher in energy than the κ^2-*N,P* isomer (the calculated Al–H stretching frequencies for this three-coordinate aluminum dihydride of 1934 and 1922 cm^{-1} were also inconsistent with experimental values). However, the κ^2-*N,N* isomer located in the PES scan was found to be very close in energy to κ^2-*N,P* **5c** (–0.8 kcal mol^{-1} more stable – DFT does not replicate the experimentally observed order of stability, though it does correctly place the two species very close in energy). Calculated Al–H stretching frequencies for κ^2-*N,P and* κ^2-*N,N* **5c** (1863, 1845 and 1860 and 1813 cm^{-1} respectively) are

sufficiently close to explain the single peak observed in the experimental solution-phase spectrum (1829 cm^{-1}).

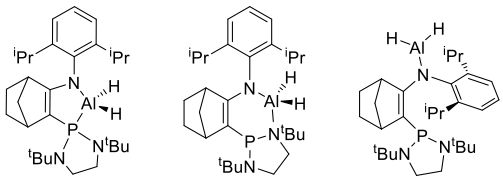


Figure 5: Computed energies of κ^2-*N,P*, κ^2-*N,N* and κ^1-*N* **5c** (M062X/6,31G+(d,p)/Lanl2DZ)

The ligand-slip rearrangement of **5c** from κ^2-*N,P* to κ^2-*N,N* is likely driven by a preference for the 'hard' nitrogen donor functionality of the diaminophosphine donor over the 'softer' phosphorus center. The increased proportion of the κ^2-*N,N* isomer for the dimethyl-complex **3c** compared to the dihydride **5c** suggests that the ring-expansion that occurs as a consequence of the isomerization from κ^2-*N,P to* κ^2-*N,N* may also be favorable as a route to relieve steric strain. The more restrained, sterically crowded, and less basic (due to the silyl substituent) tert-butyl amino groups of **3b** and **5b** cannot favorably participate in the same isomerization as **3c** and **5c**.

Interconversion between κ^2-*N,P* and κ^2-*N,N* **3c** or **5c** in solution was not observable, and we were thus unable to determine activation barriers for this process. Although resonances for the coordinated and free phosphine centers in both isomers of **5c** are broad, using NMR spectroscopy, we could find no evidence for exchange between the two sites, even at elevated temperatures. The variable coordination mode of the ligand in both **3c** and **5c** appears to provide them with higher reactivity and renders them the most sensitive derivatives in these series. Indeed, **3c** was found to be extremely challenging to handle due to its high sensitivity to air and moisture.

Solid State NMR Spectroscopy. To further confirm our assignment of ^{31}P resonances for the κ^2-*N,P* and κ^2-*N,N* isomers of **3c** and **5c**, we undertook solid-state NMR spectroscopy, since from crystallographic studies κ^2-*N,P*-coordination is exclusively observed. The MAS $^{31}P\{^1H\}$ NMR spectra of **3c** and **5c** are consistent with X-ray crystallography, revealing only a single phosphorus environment for each compound (Figure 5). In both cases the solid-state chemical shift is almost identical to the solution phase signal assigned to the κ^2-*N,P* isomers (e.g. **3c** solid phase: 47.8 ppm, solution: 49.7 ppm; **5c** solid phase: 47.5 ppm, solution: 47.8 ppm). Furthermore, the lineshapes observed in the $^{31}P\{^1H\}$ NMR spectra indicate quadrupolar coupling between aluminum and phosphorus, explaining the observed variation from the expected 1:1:1:1:1:1 sextet. No other resonances were observed in the $^{31}P\{^1H\}$ MAS NMR spectra, ruling out the presence of the κ^2-*N,N*-isomer in the solid state.

For **3a-b** and **5a-b**, which all display exclusive κ^2-*N,P* coordination in solution, the observed MAS $^{31}P\{^1H\}$ NMR spectra each contain a single resonance extremely close in chemical shift to that observed in solution (e.g. **5a** solution phase: 8.0 ppm, solid phase: 8.9 ppm). Although we were unable to observe any resonances for any of the compounds reported here by solution-phase ^{27}Al NMR spectroscopy, solid-state experiments were more successful. Details of $^{27}Al\{^1H\}$ CPMG NMR spectra for **3a-c** and **5a-c** are provided in the Supporting Information.

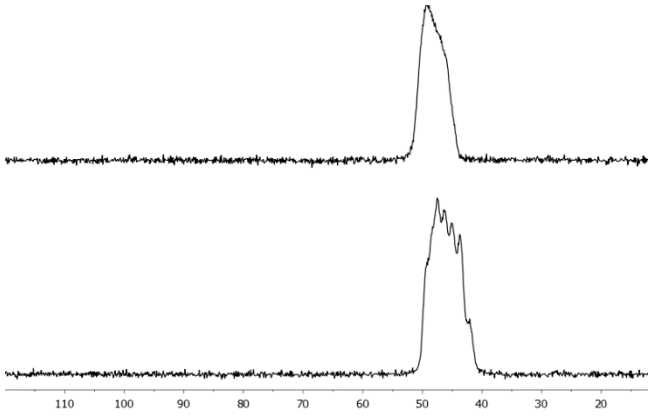
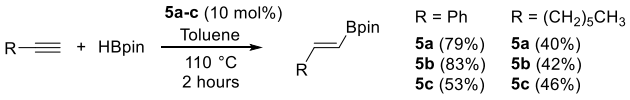


Figure 5: $^{31}P\{^{1}H\}$ (9.4 T, 14 kHz MAS) NMR spectrum for **3c** (top) and **5c** (bottom)

Conclusions

In summary, we have synthesized aluminum dimethyl and dihydride complexes with a series of amido-phosphine ligands of varying steric bulk. The bulky bidentate ligands **1a-c** enable the isolation of reactive aluminum dihydrides, the synthesis of which was observed to proceed through five-coordinate aluminate intermediates (**4a-c**). Evidence from X-ray crystallography and solid state NMR spectroscopy indicates that for all dimethyl and dihydride complexes, both nitrogen and phosphorus donor atoms are bound to the aluminum centers in the solid state. In solution, however, altering the steric bulk of the ligand enables control over coordination mode at the aluminum center: for the bulkiest ligand employed – **1c** – both the dimethyl and dihydride complexes **3c** and **5c** exist as a mixture of κ^2-*N,P* and κ^2-*N,N* isomers.



Scheme 5: Catalytic hydroboration of phenylacetylene and 2-cyclooctyne using **5a-c**.

The variable coordination mode of the ligand is encouraging as a potential route to control the stoichiometric or catalytic reactivity of the aluminum dihydride centers. For example, preliminary results indicate that **5a**-**5c** are active catalysts for the hydroboration of alkyl- and aryl-alkynes with

HBPin (see SI). The accessibility of the κ^2-*N,N* coordination mode for **5c** has a clear effect on reactivity. Whilst all three dihydrides catalyze the hydroboration of phenylacetylene with HBPin, **5a** and **5b** are significantly more efficient, with conversions of 79 and 83 % after 2 hours at 110 ºC compared to 53 % for **5c**. We are now further exploring the coordination chemistry, reactivity and catalytic applications of the dihydrides **5a-c.**

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. Reactions were carried out in glass Schlenk tubes, which were dried for 16 hours at 110 °C before use. Solvents were obtained from an inert solvent purification system and stored over 4 Å molecular sieves. C_6D_6 and d_8-THF were dried over potassium then vacuum distilled and stored over 4 Å molecular sieves.

Ligands **1b** and **1c**[23], their precursors (imine[24], chlorophosphines $PCl(N^tBu)_2SiMe_2$[23] and $PCl(N^tBuCH_2)_2$[35]) and $[H_3Al{\cdot}NMe_3]$[36] were synthesised according to literature procedures. $SiMe_2(NH^tBu)_2$ was synthesised according to a modified literature procedure (See Supporting Information). *Tert*-butylamine was dried over calcium hydride and vacuum distilled prior to use. $LiAlH_4$ was purified by extraction with diethyl ether and filtration to afford a white solid, which was stored under an inert atmosphere. Trimethylammonium chloride was dried under vacuum at 50 °C for 3 hours prior to use. All other reagents were purchased from commercial suppliers and used without further purification.

General Synthesis of 2. To a solution of **1** in THF cooled to -78 °C, ^{n}BuLi (2.5M in hexanes, 1 equivalent) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. Monitoring by $^{31}P\{^{1}H\}$ NMR spectroscopy revealed the presence of lithiated ligand **2**, which was characterised *in situ*.

2a. $^{31}P\{^{1}H\}$ (C_4H_8O, 202.5 MHz, 300 K): δ 10.9 (1:1:1:1 quartet, $J_{P\text{-}Li}$ = 54 Hz); **^{7}Li (C_4H_8O, 194.4 MHz, 300 K):** δ 1.3 (d, $J_{Li\text{-}P}$ = 54 Hz)

2b. $^{31}P\{^{1}H\}$ (C_4H_8O, 202.5 MHz, 300 K): δ 96.4 (1:1:1:1 quartet, $J_{P\text{-}Li}$ = 63 Hz); **^{7}Li (C_4H_8O, 194.4 MHz, 300 K):** δ 1.1 (d, $J_{Li\text{-}P}$ = 63 Hz)

2c. $^{31}P\{^{1}H\}$ (C_4H_8O, 202.5 MHz, 300 K): δ 68.6 (1:1:1:1 quartet, $J_{P\text{-}Li}$ = 54 Hz); **^{7}Li (C_4H_8O, 194.4 MHz, 300 K):** δ 1.5 (d, $J_{Li\text{-}P}$ = 54 Hz)

General Syntheses of 3. To a solution of **1** in THF cooled to -78 °C, ^{n}BuLi (2.5M in hexanes, 1 equivalent) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and Me_2AlCl (1.0 M in hexanes) was added dropwise. The cold bath was removed and the resultant solution was stirred at room temperature for 1 hour. The solvent was removed *in vacuo*, the product extracted in hexane and dried to afford **3a-c**.

3a: **1a** (0.40 g, 0.97 mmol), THF (20 mL), ^{n}BuLi (0.39 mL, 0.97 mmol, 1.0 eq), Me_2AlCl (0.97 mL, 0.97 mmol, 1.0 eq) yielded **3a** (0.34 g, 75%) as a pale yellow solid. Colourless crystals suitable for X-ray crystallography were grown from a saturated diethyl ether solution at 4 °C.

^{1}H (C_6D_6, 500 MHz, 300 K): δ -0.33 (d, $^{3}J_{HP}$ = 2.5 Hz, 3H, $AlCH_3$), -0.19 (d, $^{3}J_{HP}$ = 2.5 Hz, 3H, $AlCH_3$), 1.10 (m, 1H, ½CH_{2Norb}), 1.19 (d, $^{3}J_{HP}$ = 8.6 Hz, 9H, CH_{3tBu}), 1.22 (d, $^{3}J_{HP}$ = 8.6 Hz, 9H,

CH_{3tBu}), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH_{3iPr}), 1.43 (m, 2H, $CH_{2CbridgeheadCP}$), 1.55 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.61 (m, 1H, ½CH_{2Norb}), 1.66 (m, 1H, ½$CH_{2CbridgeheadCN}$), 2.50 (br s, 1H, $PCCH_{bridgehead}$), 2.95 (br s, 1H, $NCCH_{bridgehead}$), 3.44 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.61 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 7.17-7.19 (m, 3H, $H_{aromatic}$); **^{13}C (C_6D_6, 126 MHz, 300 K):** δ -5.7 (br s, $AlCH_3$), -4.3 (br s, $AlCH_3$), 25.2 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.7 (s, CH_{3iPr}), 25.8 (s, CH_{3iPr}), 25.9 (d, J_{CP} = 2 Hz, $CH_{2CbridgeheadCP}$), 27.6 (s, CH_{iPr}), 27.7 (s, CH_{iPr}), 30.0 (s, $CH_{2CbridgeheadCN}$), 30.1 (d, J_{CP} = 5 Hz, CH_{3tBu}), 30.5 (d, J_{CP} = 5 Hz, CH_{3tBu}), 34.4 (d, J_{CP} = 30 Hz, C^tBu), 34.8 (d, J_{CP} = 31 Hz, C^tBu), 43.8 (d, J_{CP} = 9 Hz, PC*C*H), 44.1 (d, J_{CP} = 2 Hz, NC*C*H), 48.3 (d, J_{CP} = 3 Hz, CH_{2Norb}), 80.2 (d, J_{CP} = 42 Hz, P*C*CH), 124.2 (s, C_{meta}), 124.3 (s, C_{meta}), 126.1 (s, C_{para}), 141.7 (d, J_{CP} = 3 Hz, NC_{Ar}), 147.1 (s, *C*CH_{iPr}), 147.4 (s, *C*CH_{iPr}), 185.1 (d, J_{CP} = 21 Hz, N*C*CH); **^{31}P{^{1}H} (C_6D_6, 162 MHz, 300 K):** δ 1.6 (s, $\Delta\nu_{½}$ = 21.1 Hz); **High Resolution Mass Spec (APPI):** m/z = 469.341919 $[C_{29}H_{49}AlNP]^+$ (theoretical = 469.341252); **Elemental Analysis:** Found (%): C, 74.13; H, 10.38; N, 2.85. Calc. for $C_{29}H_{49}AlNP$: C, 74.16; H, 10.52; N, 2.98.

3b: **1b** (0.3 g, 0.60 mmol), THF (20 mL), ^{n}BuLi (0.24 mL, 0.60 mmol, 1.0 eq), Me_2AlCl (0.60 mL, 0.60 mmol, 1.0 eq) yielded **3b** (0.17 g, 56%) as a yellow solid. Some impurities (less than 10%) were observed by NMR spectroscopy due to reaction with water, but could not be separated since crystallisation of **3b** was not possible.

^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ -0.26 (d, $^3J_{HP}$ = 3.9 Hz, 3H, $AlCH_3$), -0.12 (d, $^3J_{HP}$ = 3.9 Hz, 3H, $AlCH_3$), 0.27 (s, 3H, $SiCH_3$), 0.32 (s, 3H, $SiCH_3$), 1.12 (d, $^2J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.25 (s, 9H, CH_{3tBu}), 1.26 (s, 9H, CH_{3tBu}), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.42 (m, 2H, $CH_{2CbridgebeadCP}$), 1.60 (d, $^2J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.69 (m, 2H, $CH_{2CbridgeheadCN}$), 2.53

(br s, 1H, $CH_{bridgeheadCP}$), 3.13 (br s, 1H, $CH_{bridgeheadCN}$), 3.51 (sept, $^3J_{HH}$ = 6.8 Hz, CH_{iPr}), 3.70 (sept, $^3J_{HH}$ = 6.8 Hz, CH_{iPr}) 7.11-7.21 (m, 3H, $H_{aromatic}$); **^{13}C NMR (C_6D_6, 126 MHz, 300 K):** δ -6.3 (br d, J_{CP} = 24.8 Hz, $AlCH_3$), -5.4 (br d, J_{CP} = 19.9 Hz, $AlCH_3$), 4.6 (d, J_{CP} = 1.4 Hz, $SiCH_3$), 6.7 (d, J_{CP} = 3.7 Hz, $SiCH_3$), 25.3 (s, CH_{3iPr}), 25.4 (s, CH_{3iPr}), 25.6 (s, CH_{3iPr}), 26.0 (s, CH_{3iPr}), 26.3 (s, $CH_{2CbridgeheadCP}$), 27.6 (s, CH_{iPr}), 27.8 (s, CH_{iPr}), 29.4 (s, $CH_{2CbridgeheadCN}$), 32.3 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 4.9 Hz, CH_{3tBu}), 40.6 (d, J_{CP} = 3.5, *C*HCN), 44.3 (d, J_{CP} = 43.9, *C*HCP), 46.6 (d, J_{CP} = 4.7 Hz, CH_{2Norb}), 50.8 (d, J_{CP} = 3.9 Hz, *C*^{t}Bu), 50.9 (d, J_{CP} = 2.8 Hz, *C*^{t}Bu), 99.1 (d, J_{CP} = 29.2 Hz, P*C*CH), 124.3 (s, C_{meta}), 124.3 (s, C_{meta}), 126.3 (s, C_{para}), 141.2 (d, J_{CP} = 3.1 Hz, NC_{Ar}), 146.6 (s, *C*CH_{iPr}), 147.0 (s, *C*CH_{iPr}), 186.8 (d, J_{CP} = 33.9 Hz, N*C*CH); **^{31}P{^{1}H} (C_6D_6, 162 MHz, 300 K):** δ 64.0 (s, $\Delta\nu_{½}$ = 35.8 Hz); **High Resolution Mass Spec (APPI):** m/z = 555.371654 $[C_{31}H_{55}AlN_3PSi]^+$ (theoretical = 555.371277).

3c: 1c (0.43 g, 0.92 mmol), THF (20 mL), ^{n}BuLi (0.37 mL, 0.92 mmol, 1.0 eq), Me_2AlCl (0.92 mL, 0.60 mmol, 1.0 eq). To gain analytically pure material, **3c** was further purified by recrystallization from hexanes at -20 °C to yield colourless crystals (0.23 g, 48%). Two isomers were identified in the NMR spectra of approximate ratio of 4:3 of κ^2-*N,N* **3c** to κ^2-*N,P* **3c** at 300 K (determined from the ^{1}H NMR spectrum). Due to the high air-sensitivity of this species, some impurities were observed in solution NMR spectra (^{31}P{^{1}H} NMR spectrum, 10% unidentified impurity at 75.1 ppm).

κ^2-*N,N* **3c**: **^{1}H (C_6D_6, 500 MHz, 300 K):** δ -0.67 (s, 3H, AlMe), -0.13 (s, 3H, AlMe), 0.89 (m, 1H, ½CH_{2Norb}), 1.18 (m, 1H, ½CH_{2Norb}), 1.21 (s, 18H, CH_{3tBu}), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (m, 2H, $CH_{2CbridgeheadCP}$), 1.47 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.63 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.72 (m, 1H, ½$CH_{2CbridgeheadCN}$), 2.49 (br s, 1H, $CH_{bridgeheadCP}$), 2.82 (m, 1H, ½NCH_2), 2.83 (m, 1H, ½NCH_2), 2.97 (m, $CH_{bridgeheadCN}$), 3.15 (m, 1H,

½NCH$_2$), 3.73 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH$_{iPr}$), 3.85 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH$_{iPr}$), 3.88 (m, 1H, ½NCH$_2$), 7.15-7.20 (m, 3H, H$_{aromatic}$); **^{13}C (C$_6$D$_6$, 126 MHz, 300 K):** δ -5.5 (s, AlMe), -4.7 (s, AlMe), 24.3 (s, CH$_{3iPr}$), 24.8 (s, CH$_{3iPr}$), 25.75 (s, CH$_{3iPr}$), 25.97 (s, CH$_{2CHbridgeheadCP}$), 26.1 (s, CH$_{3iPr}$), 27.0 (s, CH$_{iPr}$), 28.2 (s, CH$_{iPr}$), 29.3 (s, CH$_{2CbridgeheadCN}$), 29.7 (d, J_{CP} = 9.5 Hz, CH$_{3tBu}$), 29.73 (d, J_{CP} = 7.7 Hz, CH$_{3tBu}$), 29.8 (d, J_{CP} = 5.6 Hz, CH$_{3tBu}$), 43.84 (s, CH$_{2Norb}$), 43.88 (d, J_{CP} = 12.6 Hz, NCH$_2$), 45.3 (s, CH$_{bridgeheadCP}$), 45.7 (d, J_{CP} = 42.0 Hz, CH$_{bridgeheadCN}$), 48.8 (d, J_{CP} = 2.8 Hz, NCH$_2$), 53.2 (d, J_{CP} = 6.0 Hz, *C*^{t}Bu), 63.7 (d, J_{CP} = 11.7 Hz, *C*^{t}Bu), 103.5 (d, J_{CP} = 37.7 Hz, P*C*CH), 123.9 (s, C$_{meta}$), 124.5 (s, C$_{meta}$), 125.2 (s, C$_{para}$), 144.1 (s, N*C*$_{Ar}$), 146.5 (s, *C*CH$_{iPr}$), 147.0 (s, *C*CH$_{iPr}$), 165.0 (d, J_{CP} = 5.0 Hz, N*C*CH); **^{31}P{^{1}H} (C$_6$D$_6$, 162 MHz, 300 K):** δ 99.9 (s, $\Delta\nu_{½}$ = 5.3 Hz).

κ^2-*N,P* **3c**: **^{1}H (C$_6$D$_6$, 500 MHz, 300 K):** δ -0.27 (d, $^3J_{HP}$ = 3.1 Hz, 3H, AlMe), -0.14 (d, $^3J_{HP}$ = 3.1 Hz, 3H, AlMe), 1.06 (dm, $^2J_{HH}$ = 8.1 Hz, 1H, ½CH$_{2Norb}$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_{3iPr}$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_{3iPr}$), 1.30 (s, 9H, CH$_{3tBu}$), 1.32 (s, 9H, CH$_{3tBu}$), 1.33 (m, 1H, ½CH$_{2CbridgeheadCP}$), 1.38 (m, 1H, ½CH$_{2CbridgeheadCP}$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_{3iPr}$), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_{3iPr}$), 1.56 (m, $^2J_{HH}$ = 8.1 Hz, 1H, ½CH$_{2Norb}$), 1.63 (m, 2H, CH$_{2CbridgeheadCN}$), 2.48 (br s, 1H, CH$_{bridgeheadCP}$), 2.59 (m, 1H, ½NCH$_2$), 2.66 (m, 1H, ½NCH$_2$), 2.82 (m, 1H, ½NCH$_2$), 2.89 (m, 1H, NCH$_2$), 3.05 (br s, 1H, CH$_{bridgeheadCN}$), 3.52 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH$_{iPr}$), 3.74 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH$_{iPr}$), 7.15-7.20 (m, 3H, H$_{aromatic}$); **^{13}C (C$_6$D$_6$, 126 MHz, 300 K):** δ -4.2 (s, AlMe), -3.5 (s, AlMe), 25.2 (s, CH$_{3iPr}$), 25.4 (s, CH$_{3iPr}$), 25.68 (s, CH$_{3iPr}$), 25.84 (s, CH$_{2CbridgeheadCP}$), 27.4 (s, CH$_{iPr}$), 27.6 (s, CH$_{iPr}$), 29.2 (s, CH$_{3tBu}$), 29.4 (d, J_{CP} = 2.2 Hz, CH$_{2CbridgeheadCN}$), 29.7 (d, J_{CP} = 7.6 Hz, CH$_{3tBu}$), 42.0 (d, J_{CP} = 4.2 Hz, CH$_{bridgeheadCN}$), 43.6 (s, NCH$_2$), 44.2 (d, J_{CP} = 9.9 Hz, CH$_{bridgeheadCP}$), 44.3 (s, NCH$_2$), 46.6 (d, J_{CP} = 5.3 Hz, CH$_{2Norb}$), 52.5 (d, J_{CP} = 11.7 Hz, *C*^{t}Bu), 52.8 (d, J_{CP} = 8.8 Hz, *C*^{t}Bu), 95.5 (d, J_{CP} = 33.5 Hz, P*C*CH), 124.29 (s,

C_{meta}), 124.32 (C_{meta}), 126.2 (s, C_{para}), 142.0 (d, J_{CP} = 3.9 Hz, NC_{Ar}), 146.7 (s, CCH_{3iPr}), 148.0 (s, CCH_{3iPr}), 185.3 (d, J_{CP} = 34.1 Hz, NCCH); **$^{31}P\{^{1}H\}$ (C_6D_6, 162 MHz, 300 K):** δ 49.7 (s, $\Delta\nu_{½}$ = 47.5 Hz); **High Resolution Mass Spec (EI):** m/z = 525.37703 $[C_{31}H_{53}AlN_3P]^+$ (theoretical = 525.37871); **Elemental Analysis:** Found (%): C, 70.71; H, 10.18; N, 8.03. Calc. for $C_{31}H_{53}AlN_3P$: C, 70.82; H, 10.16; N, 7.99.

Synthesis of 4b. To a solution of **1b** (0.10 g, 0.2 mmol) in THF (20 mL) at -78 °C, ^{n}BuLi (2.5 M in hexanes, 0.08 mL, 0.2 mmol, 1 eq) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and $H_3Al{\cdot}NMe_2Et$ (0.5M in toluene, 0.4 mL, 1 eq) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 20 minutes and the solvent removed *in vacuo* to afford the product as a yellow oil. No further purification was attempted.

^{1}H NMR (C_4D_8O, 500 MHz, 300 K): δ 0.29 (s, 3H, $SiCH_3$), 0.33 (s, 3H, $SiCH_3$), 0.84 (m, 1H, ½CH_{2Norb}), 1.07 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.08 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.12 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.14 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.18 (m, 2H, $CH_{2CbridgeheadCP}$), 1.19 (s, 9H, CH_{3tBu}), 1.21 (s, 9H, CH_{3tBu}), 1.25 (m, 1H, ½CH_{2Norb}), 1.54 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.62 (m, 1H, ½$CH_{2CbridgheadCN}$), 2.19 (br s, 1H, $CH_{bridgeheadCP}$), 3.35 (br s, 1H, $CH_{bridgeheadCN}$), 3.54 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.63 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 6.83-6.90 (m, 3H, $H_{aromatic}$). Note: It was not possible to locate the Al-H resonances even with the use of $^{1}H\{^{31}P\}$ NMR experiments, likely due to extremely high linewidth. **^{13}C NMR (C_4D_8O, 126 MHz, 300 K):** δ 6.5 (s, $SiCH_3$), 8.3 (d, J_{CP} = 5.7 Hz, $SiCH_3$), 24.3 (d, J_{CP} = 10.2 Hz, CH_{3iPr}), 26.0 (d, J_{CP} = 15.2 Hz, CH_{3iPr}), 27.2 (s, $CH_{2CbridgeheadCP}$), 28.11 (s, CH_{iPr}), 28.13 (s, CH_{iPr}), 30.1 (s, $CH_{2CbridgeheadCN}$), 32.9 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 33.4 (d, J_{CP} = 4.8 Hz, CH_{3tBu}), 42.1 (d, J_{CP} = 1.5 Hz, $CH_{bridgeheadCN}$), 46.5 (s, CH_{2Norb}),

47.2 (d, J_{CP} = 5.5 Hz, $CH_{bridgeheadCP}$), 51.4 (d, J_{CP} = 11.5 Hz, $C^{t}Bu$), 51.6 (d, J_{CP} = 14.6 Hz, $C^{t}Bu$), 111.2 (d, J_{CP} = 43.1 Hz, P*C*CH), 123.1 (d, J_{CP} = 10.0 Hz, C_{meta}), 124.2 (s, C_{para}), 146.7 (s, *C*CH_{iPr}), 148.0 (s, *C*CH_{iPr}), 150.7 (s, NC_{Ar}), 174.2 (d, J_{CP} = 33.2 Hz, N*C*CH); **^{31}P (C_4D_8O, 162 MHz, 300 K):** δ 110.8 (q, $^{2}J_{PH}$ = 34 Hz); **^{7}Li (C_4D_8O, 194.4 MHz, 300 K):** δ -0.43 (s); **High Resolution Mass Spec (EI):** m/z = 528.34912 $[C_{29}H_{52}N_3AlPSi]^+$ (theoretical = 528.34891).

General Synthesis of 5. To a solution of ligand **1a-c** in THF cooled to -78 °C, ^{n}BuLi (2.5M in hexanes) was added dropwise. The cold bath was removed and the resultant yellow solution was stirred at room temperature for 1 hour. The reaction mixture was cooled to -78 °C and a solution of $H_3Al{\cdot}NMe_3$ in THF was added dropwise. The cold bath was removed and the resultant colourless solution was stirred at room temperature for 1 hour. The solvent was removed *in vacuo*, the product extracted in hexane and dried to afford a white solid. $H_3Al{\cdot}NMe_2Et$ (0.5 M in toluene) can be used in place of $H_3Al{\cdot}NMe_3$. In this work, $H_3Al{\cdot}NMe_2Et$ was used for initial test reactions to synthesise up to 0.2 g of **5** using an identical procedure to that described above.

5a: 1a (1.63 g, 0.0039 mol), THF (50 mL), ^{n}BuLi (1.6 mL, 0.0039 mol, 1.0 eq), $H_3Al{\cdot}NMe_3$ (0.84 g, 0.0037 mol, 2.4 eq) in THF (20 mL) yielded **5a** (1.57 g, 91%).

^{1}H (C_6D_6, 500 MHz, 300 K): δ 1.11 (dm, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.19 (d, $^{3}J_{HP}$ = 14.2 Hz, 9H, CH_{3tBu}), 1.22 (d, $^{3}J_{HP}$ = 14.2 Hz, 9H, CH_{3tBu}), 1.28 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.29 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (m, 2H, $CH_{2CbridgeheadCP}$), 1.42 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.44 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.51 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.62 (dm, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.67 (m, 1H, ½$CH_{2CbirdgeheadCN}$), 2.53 (br s, 1H, $PCCH_{bridgehead}$), 2.94 (br s, 1H, $NCCH_{bridgehead}$), 3.42 (sept, $^{3}J_{HH}$ = 6.8 Hz, CH_{iPr}), 3.63 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, AlH_2), 7.16-7.22 (m, 3H, $H_{aromatic}$); **^{13}C (C_6D_6, 126 MHz, 300 K):** δ 24.0 (s, CH_{3iPr}), 24.7 (s,

CH_{3iPr}), 25.2 (d, J_{CP} = 1.8 Hz, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.9 (s, CH_{3iPr}), 28.0 (s, CH_{iPr}), 28.1 (s, CH_{iPr}), 29.6 (d, J_{CP} = 4.5 Hz, CH_{3tBu}), 30.1 (s, $CH_{2CbridgeheadCN}$), 30.1 (d, J_{CP} = 4.0 Hz, CH_{3tBu}), 34.1 (d, J_{CP} = 18.2 Hz, $C^{t}Bu$), 34.3 (d, J_{CP} = 18.9 Hz, $C^{t}Bu$), 43.6 (d, J_{CP} = 9.1 Hz, $CH_{bridgeheadCP}$), 44.1 (d, J_{CP} = 2.1 Hz, $CH_{bridgeheadCN}$), 48.6 (d, J_{CP} = 3.9 Hz, CH_{2Norb}), 81.0 (d, J_{CP} = 44.5 Hz, P*C*CH), 124.1 (s, C_{meta}), 124.2 (s, C_{meta}), 126.3 (s, C_{para}), 141.4 (d, J_{CP} = 3.0 Hz, N*C*$_{Ar}$), 146.8 (s, *C*CH_{iPr}), 147.1 (s, *C*CH_{iPr}), 185.1 (d, J_{CP} = 20.1 Hz, N*C*CH); **$^{31}P\{^{1}H\}$ (C_6D_6, 162 MHz, 300 K):** δ 8.0 (s, $\Delta\nu_{½}$ = 34.7 Hz); **High Resolution Mass Spec (EI):** m/z = 441.30855 $[C_{27}H_{45}AlNP]^{+}$ (theoretical = 441.30996); **Elemental Analysis:** Found (%): C, 73.11; H, 10.39; N, 3.13. Calc. for $C_{27}H_{45}AlNP$: C, 73.43; H, 10.27; N, 3.17; **IR (solid, cm^{-1}):** 1810, 1786; **IR (solution, cm^{-1}):** 1811.

5b: **1b** (3.00 g, 0.0060 mol), THF (80 mL), ^{n}BuLi (2.4 mL, 0.0060 mol, 1.0 eq), $H_3Al{\cdot}NMe_3$ (1.28 g, 0.014 mol, 2.4 eq) in THF (15 mL) yielded **5b** (2.95 g, 93%). Colourless crystals suitable for X-ray crystallography were grown from a saturated hexane solution at -20 °C.

^{1}H NMR (C_6D_6, 500 MHz, 300 K): δ 0.24 (s, 3H, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$), 1.13 (d, $^{2}J_{HH}$ = 8.1 Hz, 1H, ½CH_{2Norb}), 1.28 (d, $^{4}J_{HP}$ = 0.8 Hz, 9H, CH_{3tBu}), 1.29 (d, $^{4}J_{HP}$ = 0.8 Hz, 9H, CH_{3tBu}), 1.30 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.38 (m, 2H, $CH_{2CbridgeheadCP}$), 1.44 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.62 (d, $^{2}J_{HH}$ = 8.1 Hz, ½CH_{2Norb}), 1.67 (m, 2H, $CH_{2CbridgeheadCN}$), 2.57 (br s, 1H, $CH_{bridgeheadCP}$), 3.12 (br s, 1H, $CH_{bridgeheadCN}$), 3.53 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.74 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, Al-H), 7.17-7.23 (m, 3H, $H_{aromatic}$); **^{13}C NMR (C_6D_6, 126 MHz, 300 K):** δ 4.4 (d, J_{CP} = 1.6 Hz, $SiCH_3$), 6.3 (d, J_{CP} = 3.2 Hz, $SiCH_3$), 24.1 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 25.6 (d, J_{CP} = 1.0 Hz, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.9 (s, CH_{3iPr}), 28.0 (s, CH_{iPr}), 28.3 (s, CH_{iPr}), 29.3 (s, $CH_{2CHbridgheadCN}$), 32.3 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 5.2, CH_{3tBu}), 40.7 (d, J_{CP} = 3.9 Hz,

$CH_{bridgheadCN}$), 43.9 (d, J_{CP} = 9.7 Hz, $CH_{bridgheadCP}$), 46.8 (d, J_{CP} = 4.9 Hz, CH_{2Norb}), 51.4 (d, J_{CP} = 2.5 Hz, $C^{t}Bu$), 51.5 (d, J_{CP} = 3.6 Hz, $C^{t}Bu$), 99.7 (d, J_{CP} = 32.6 Hz, P*C*CH), 124.1 (s, C_{meta}), 124.2 (s, C_{meta}), 126.5 (s, C_{para}), 140.8 (d, J_{CP} = 3.5 Hz, NC_{Ar}), 146.4 (s, $C_{Ar}CH_{iPr}$), 146.5 (s, $C_{Ar}CH_{iPr}$), 187.6 (d, J_{CP} = 33.9 Hz, N*C*CH); **$^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz, 300 K):** δ 61.3 (s, $\Delta\nu_{½}$ = 65.4 Hz); **High Resolution Mass Spec (EI):** m/z = 527.33886 $[C_{29}H_{51}AlN_3PSi]^+$ (theoretical = 527.33998); **Elemental Analysis:** Found (%): C, 65.95; H, 9.66; N, 7.83. Calc. for $C_{29}H_{51}AlN_3PSi$: C, 66.00; H, 9.74; N, 7.96; **IR (solid, cm^{-1}):** 1831, 1816; **IR (solution, cm^{-1}):** 1820.

5c: 1c (2.00 g, 0.0043 mol), THF (100 mL), $^{n}BuLi$ (1.7 mL, 0.0043 mol, 1.0 eq), $H_3Al{\cdot}NMe_3$ (0.91 g, 0.010 mol, 2.4 eq) in THF (15 mL). The final product was further purified by recrystallization from hexanes at -20 °C to yield **5c** as colourless crystals (1.68 g, 79%). Two isomers were identifiable in the solution phase NMR spectra in a ratio of 4:7 for κ^2-*N,N* **5c** to κ^2-*N,P* **5c** at 300 K (determined from the ^{1}H NMR spectrum).

κ^2-*N,N* **5c: ^{1}H (C_6D_6, 500 MHz, 300 K):** δ 0.91 (m, 1H, ½CH_{2Norb}), 1.18 (d, $^{4}J_{HP}$ = 1.3 Hz, 9H, CH_{3tBu}), 1.23 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.25 (m, 1H, ½CH_{2Norb}), 1.31 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_{3iPr}), 1.32 (s, 9H, CH_{3tBu}), 1.43 (m, 2H, $CH_{2CbridgeheadCP}$), 1.60 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.65 (m, 1H, ½$CH_{2CbridgeheadCN}$), 1.71 (m, 1H, ½$CH_{2CbridgeheadCN}$), 2.56 (m, 1H, $CH_{bridgeheadCP}$), 2.70 (m, 1H, ½NCH_2), 2.78 (m, 1H, ½NCH_2), 2.97 (m, 1H, $CH_{bridgeheadCN}$), 3.33 (m, 1H, ½NCH_2), 3.56 (m, 1H, ½NCH_2), 3.85 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.98 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.3 (br s, 2H, AlH_2) 7.18-7.21 (m, 3H, $H_{aromatic}$); **^{13}C (C_6D_6, 126 MHz, 300 K):** δ 25.4 (s, $CH_{2CbridgeheadCP}$), 25.6 (s, CH_{3iPr}), 25.7 (s, CH_{3iPr}), 25.92 (s, CH_{3iPr}), 27.5 (s, CH_{iPr}), 28.9 (s, CH_{iPr}), 29.0 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 29.6 (d, J_{CP} = 10.7 Hz, CH_{3tBu}), 29.8 (d, J_{CP} = 1.8 Hz, $CH_{2CbridgeaheadCN}$), 44.2 (s, CH_{2Norb}), 45.1 (s, $CH_{bridgeheadCN}$), 45.7 (s, NCH_2), 45.8 (d, J_{CP} = 39.1 Hz,

$CH_{bridgeheadCP}$), 48.8 (d, J_{CP} = 3.3 Hz, NCH_2), 53.5 (d, J_{CP} = 5.0 Hz, C^tBu), 53.8 (d, J_{CP} = 3.9 Hz, C^tBu), 104.8 (d, J_{CP} = 36.9 Hz, P*C*CH), 123.9 (s, C_{meta}), 124.6 (s, C_{meta}), 125.2 (s, C_{para}), 143.22 (s, NC_{Ar}), 145.8 (*C*CH_{iPr}), 146.53 (s, *C*CH_{iPr}), 167.4 (d, J_{CP} = 2.7 Hz, N*C*CH); **$^{31}P\{^1H\}$ (C_6D_6, 162 MHz, 300 K):** δ 96.9 (s, $\Delta\nu_{½}$ = 137.9 Hz).

κ^2-*N,P* **5c: ^{1}H (C_6D_6, 500 MHz, 300 K):** δ 1.07 (dm, $^2J_{HH}$ = 8.4 Hz, 1H, ½CH_{2Norb}), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.32 (s, 9H, CH_{3tBu}), 1.35 (s, 9H, CH_{3tBu}), 1.39 (m, 2H, $CH_{2CbridgeheadCP}$), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.56 (m, 1H, ½CH_{2Norb}), 1.63 (m, 2H, $CH_{2CbridgeheadCN}$), 2.52 (m, 1H, $CH_{bridgeheadCP}$), 2.60 (m, 1H, ½NCH_2), 2.72 (m, 1H, ½NCH_2), 2.79 (m, 1H, ½NCH_2), 2.88 (m, 1H, NCH_2), 3.02 (m, 1H, $CH_{bridgeheadCN}$), 3.54 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 3.76 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{iPr}), 4.6 (br s, 2H, AlH_2) 7.18-7.21 (m, 3H, $H_{aromatic}$); **^{13}C (C_6D_6, 126 MHz, 300 K):** δ 24.0 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 25.3 (s, $CH_{2CbridgeheadCP}$), 25.8 (s, CH_{3iPr}), 25.86 (s, CH_{3iPr}), 27.9 (s, CH_{iPr}), 28.1 (s, CH_{iPr}), 29.0 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 29.3 (s, $CH_{2CbridgeheadCN}$), 29.9 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 42.7 (d, J_{CP} = 4.4 Hz, $CH_{bridgeheadCN}$), 43.6 (d, J_{CP} = 9.9 Hz, $CH_{bridgeheadCP}$), 43.9 (s, NCH_2), 44.2 (s, NCH_2), 46.6 (d, J_{CP} = 4.9 Hz, CH_{2Norb}), 53.4 (d, J_{CP} = 9.8 Hz, *C*^{t}Bu), 53.6 (d, J_{CP} = 5.4 Hz, *C*^{t}Bu), 97.0 (d, J_{CP} = 35.3 Hz, P*C*CH), 124.1 (s, C_{meta}), 124.3 (s, C_{meta}), 126.4 (s, C_{para}), 141.0 (d, J_{CP} = 4.0 Hz, NC_{Ar}), 146.51 (s, *C*CH_{iPr}), 146.8 (s, *C*CH_{iPr}), 185.4 (d, J_{CP} = 34.0 Hz, N*C*CH); **$^{31}P\{^1H\}$ (C_6D_6, 162 MHz, 300 K):** δ 47.8 (s, $\Delta\nu_{½}$ = 96.6 Hz); **High Resolution Mass Spec (EI):** m/z = 497.35079 $[C_{29}H_{49}AlN_3P]^+$ (theoretical = 497.34741); **Elemental Analysis:** Found (%): C, 69.80; H, 9.80; N, 8.33. Calc. for $C_{29}H_{51}AlN_3PSi$: C, 69.99; H, 9.92; N, 8.44; **IR (solid, cm^{-1}):** 1825, 1801; **IR (solution, cm^{-1}):** 1823.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supporting Information (Experimental procedures, full characterization of compounds, crystallographic details, solid state NMR details, solution phase NMR spectra; PDF)

AUTHOR INFORMATION

Corresponding Author

*Michael J. Cowley, michael.cowley@ed.ac.uk

Author Contributions

RLF conceived and performed experiments and co-wrote the manuscript, GSN contributed to crystallographic studies, MJC designed and coordinated the study and co-wrote the manuscript.

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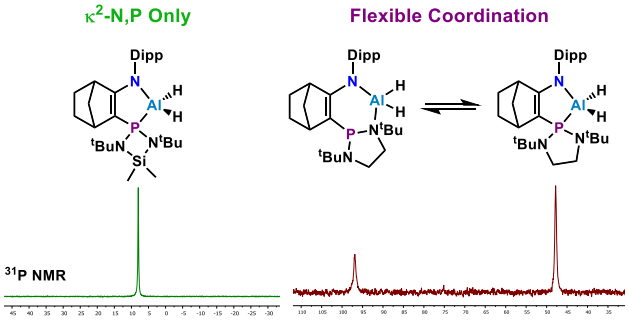
1 TOC SYNOPSIS

2 Mixed *N,P*-donor stabilized aluminum dimethyl and dihydride complexes were synthesized.
3 Variation of the ligand's phosphine donor group enables control over the coordination mode at
4 aluminum.

5 TOC Graphic:



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